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Synthesis of Nanostructured Solid-State Phases of V_7O_{16} and V_2O_5 Compounds for ppb-Level Detection of Ammonia

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Abstract

Solid state phase of V_7O_{16} with separate V_2O_5 phase were fabricated by pulsed laser deposition. The crystal structure and symmetry of the deposited films were studied with X-ray diffraction and Raman spectroscopy, respectively. Rietveld analysis was performed to the X-ray diffraction measurement results. The surface potentials and morphologies of the films were studied with atomic force microscopy, and microstructure of the thin films was analyzed by transmission electron microscopy. Raman spectroscopy and Rietveld refinement results confirmed that the thin-film crystal structures varied between orthorhombic V_2O_5 phase and another phase, triclinic V_7O_{16} , previously found only in the walls of vanadium oxide nanotubes (VO_x -NT), bound together with organic amine. We have earlier presented the first results of stable and pure metal-oxide solid-state phase of V_7O_{16} manufactured from ceramic V_2O_5 target. Here we show more detailed study of these structures. The microstructure studies showed a variation on the porosity of the films according to crystal structures and also some fiber-like nanostructures were found in the films. The surface morphology depended strongly on the crystal structure and the surface potential studies showed ~ 50 meV difference in the work function values between the phases. Compounds were found to be extremely sensitive towards ammonia, NH_3 , down to ~ 40 ppb concentrations, and have shown to

have the stability and selectivity to control the Selective Catalytic Reduction process, where nitrogen oxides are reduced by ammonia in, *e.g.* diesel exhausts.

Keywords: Vanadium oxides; Mixed phase; V_7O_{16} ; V_2O_5 ; Thin film

1. Introduction

Vanadium oxides have gained a constantly growing interest because of their varying material properties according to oxidation state. The material can have oxidation states between V^{2+} and V^{5+} , the most famous compounds being vanadium pentoxide, V_2O_5 and vanadium dioxide, VO_2 . For example, vanadium dioxide has an interesting metal-insulator-transition (MIT) effect where it changes its phase structure from low-temperature insulating state to high-temperature metallic state at around 68 °C. This property has been studied in the context of, *e.g.* electrical and optical switches [1]. On the other hand, vanadium pentoxide V_2O_5 has been studied for chemical sensing purposes [2] and as a material for catalytic reactions [3]. Lately, a growing interest has been shown to fabrication of vanadium oxide nanotubes, often labelled as VO_x -NT or VONT, by chemical methods [4]. The structure of the tubes is composed of triclinic V_7O_{16} layer walls with an organic amine in between the layers [5,6]. VO_x -NTs have been studied, *e.g.* as chemical sensing material and Li^+ battery applications [7,8].

Vanadium oxides as a material group are relatively complex. They are often formed as a layered structure, *e.g.* the well-known vanadium pentoxide V_2O_5 [9] and can also exist in a more complex mixed-valence vanadium oxide form. The mixed valency occurs when oxygen vacancy defects are introduced to an ideal vanadium oxide structure. When the number of oxygen vacancies is above a certain limit, the vacancies couple and arrange along lattice planes and this is compensated by reorganization of V-O coordination units. This results in formation of related, more complex stoichiometries [10]. The often seen mixed valence oxides consisting of, *e.g.* both V^{4+} and V^{5+} ions have a crucial impact on the material properties. In our previous study, it was shown that when a thin film consists of both pure V_2O_5 phase, including only V^{5+} ions, and a mixed valency phase of

V_7O_{16} , including both V^{4+} ions and V^{5+} ions, a dramatic effect on the electrical conductivity of the thin films occurs, causing both n-type and p-type conductivity, respectively, to exist in the same samples [11]. Twin-plane crystal structure is another property present, for instance in vanadium oxide single crystals and VO_x -NT's, where the crystals are mirrored to each other with respect to a certain twin plane [12, 13]. For example, in V_7O_{16} phase, the crystals are rotational twins in the *ab*-plane, *i.e.* basal plane, of the unit cell [5]. These types of properties make vanadium oxides a very fascinating material group with possibilities to be utilized in many different kinds of applications.

Pulsed laser deposition (PLD) has been used to manufacture vanadium oxide thin films for some time [14], and it has some advantages to other methods including good repetition of stoichiometry of the target material in the films on the substrate and easy controlling the chemical composition of the films. We have previously shown the existence of a stable and pure metal oxide solid-state phase of V_7O_{16} in a thin film structure. In this study, a comprehensive structural characterization of pulsed laser deposited nanostructured mixed phase V_2O_5 and V_7O_{16} thin films was performed. It must be pointed out here, that pure vanadium pentoxide V_2O_5 films can be easily fabricated by PLD [15]. The most important result in this paper is the fabrication of pure stable solid-state phase of triclinic V_7O_{16} , even though as a mixture with V_2O_5 , and the observation of extremely low detection limit of the compound towards ammonia gas. Also, the compositions have been proven to be very stable and selective as ammonia gas sensors in Selective Catalytic Reduction (SCR) process [16], when compared to 20 ppm of NO and 50 ppm of CO.

2. Experimental

Excimer laser operating at a wavelength of 308 nm (Lambda Physik Compex 201) was used to deposit vanadium oxide thin films on *c*-cut Al_2O_3 (0001) and oxidized silicon substrates with a pulse repetition rate of 5 Hz. Pure ceramic V_2O_5 disc was used as rotating target and the laser pulse energy densities used in depositions were $I = 1.3 \text{ J/cm}^2$ and $I = 2.6 \text{ J/cm}^2$. The substrate temperatures of *in-situ* PLD processes were $T = 400 \text{ }^\circ\text{C}$ and $500 \text{ }^\circ\text{C}$. The deposition chamber was

first evacuated to a base pressure of $\sim 5 \times 10^{-5}$ mbar and then oxygen partial pressure $p(\text{O}_2) = 1 \times 10^{-2}$ mbar or 1.5×10^{-2} mbar was added in the chamber. Some samples were post annealed at 400 °C for 1h in air atmosphere.

Crystal structure of the films was studied using $\theta - 2\theta$ and grazing incidence diffraction (GID) X-ray diffraction (XRD) by Bruker D8 Discover facility, and TOPAS software was used to make Rietveld refinement for the structure data. Vesta software was used in drawing the lattice models of the crystal structures [17]. HORIBA Jobin Yvon LabRAM HR800 Raman spectroscope with argon-ion laser with a wavelength of 488 nm was used to study the phonon modes of the samples. The surface potential and morphology were studied using Veeco Dimension 3100 atomic force microscope (AFM) and WSXM software [18]. Transmission electron microscopy (TEM) studies were made using Tecnai Spirit G2 electron microscope operated at 120 kV and equipped with Quemesa CCD camera.

Platinum (Pt) electrodes with thickness of 400 nm together with 10 nm-thick titanium (Ti) adhesion layers were fabricated to the surface of the thin films by DC magnetron sputtering. Then the sensors were glued on alumina based heating platform and Pt-100 temperature sensors were used to measure the temperature of the gas sensors. The resistance measurements were performed with a Keithley sourcemeter and Bronckhorst flow meters were used to control the gas pulses injected to the 1 cm³-sized gas measurement chamber. The carrier gas used was 20 % of O₂ in N₂ and measurement temperature was 350 °C. In all gas sensing measurements, the temperature was raised rapidly to 350 °C and then the sensors were kept at the temperature for several hours in order to clean the sensor and stabilize the resistance baseline. Before the injection of ppb-level of ammonia, NH₃, to the chamber, the plastic gas tubes were replaced with new ones in order to prevent diffusion of buildup NH₃ in the gas line to affect the adjusted concentration of ammonia gas in the chamber.

3. Results and discussion

3.1 Crystal structure characterization

For exact determination of nanosized crystalline structure of the films, both Raman spectroscopy and X-ray diffraction methods were utilized. According to data shown in Fig. 1, all the films had two co-existing phases. The post annealed films, bottom curve, were composed of almost pure V_2O_5 phase [19]. Films deposited with parameters $I = 2.6 \text{ J/cm}^2$, $T = 400 \text{ }^\circ\text{C}$ and $p(O_2) = 1.5 \times 10^{-2} \text{ mbar}$, showed almost equal co-existence of V_2O_5 phase and another phase, as shown by middle curve in Fig.1. The other phase, identified by Raman modes at wavenumbers 167, 847, 882, 940 and 1034 cm^{-1} , labelled by black circles in the top curve in Fig. 1, could be identified as a structure typically found in vanadium oxide nanotubes (VO_x -NT) [20,21]. On the other hand, films deposited with PLD-parameters $I = 2.6 \text{ J/cm}^2$, $T = 500 \text{ }^\circ\text{C}$ and $p(O_2) = 1.5 \times 10^{-2} \text{ mbar}$, were almost pure VO_x -NT-phase films, as shown by the top curve in Fig. 1. In the literature, this VO_x -NT phase is always referred to triclinic V_7O_{16} structure in multilayers separated by organic amine layers in VO_x nanotubes [5,6]. Identical Raman spectra are here found in pure inorganic solid-state metal oxide films. Also, it is worth noting that all the other Raman modes in Fig. 1 originate from orthorhombic $Pmmn$ symmetry of V_2O_5 .

Figure 1. Raman spectra of the different vanadium oxide thin films. The black circles represent Raman modes typical to $\text{VO}_x\text{-NT}$ -structure formed of layers of V_7O_{16} .

Rietveld refined $\theta - 2\theta$ X-ray diffraction data of a typical mixed V_2O_5 and $\text{VO}_x\text{-NT}$ -type phase thin film is shown in Fig. 2. Raman spectrum of such a film is shown by the middle curve in Fig. 1. The XRD data was fitted with both orthorhombic $Pmmn$ symmetry in the case V_2O_5 [22] and triclinic $P-1$ symmetry in the case of V_7O_{16} [5]. It is clearly observed from Fig. 2, that Rietveld refinement calculated curve fits all the measured XRD peaks, and relates reflections from $(003)_T \dots (2,-1,2)_T$ planes to triclinic V_7O_{16} structure, and $(200)_O \dots (011)_O$ planes to orthorhombic V_2O_5 structure, respectively. It is also worth mentioning that various phases of vanadium oxides, including VO_2 , V_2O_3 , and V_4O_9 structure, were also examined without any success in fitting. The R weighted parameter, measuring the relation of the observed and calculated intensities of the measurement, was $\text{RWP} = 24.384 \%$. The closer to zero the RWP value is, the better the fit. The relatively high RWP value in this measurement is a result of a quite strong background noise.

Another parameter also used to measure the reliability of the Rietveld refinement calculation is χ^2 function, i.e. goodness-of-fit, value should be as close to 1 as possible [23]. The χ^2 function measures the relation between the gained RWP value and the expected R-value based on the measurement data. In the fitting in Fig. 2, the value of goodness-of-fit was $\chi^2 = 1.30$. Overall, these Rietveld refinement results together with Raman results confirm unambiguously that the thin films are indeed composed of both pure V_2O_5 and V_7O_{16} phases.

Figure 2. A typical $\theta - 2\theta$ X-ray diffraction pattern with Rietveld refinement calculated using structural parameters of orthorhombic V_2O_5 phase with symmetry ($pmmn$) and triclinic V_7O_{16} phase with symmetry ($P-1$).

The lattice models used in the refinement are shown in Fig. 3. The unit cell of orthorhombic $Pmmn$ V_2O_5 is composed of VO_6 octahedra structures linked from the edges by chained oxygen atoms (O3) and from the corners by bridging oxygen atoms (O1), as shown in Fig. 3 a). The unit cell of triclinic $P-1$ V_7O_{16} is composed of two weakly bonded sheets of VO_5 square pyramids combined via VO_4 tetrahedra around vanadium (V5) atom, as shown in Fig. 3 b). This form of

V_7O_{16} structure has not been reported as a stable solid-state thin-film structure before. Typical layered structure of vanadium oxides is now also seen in the structure of triclinic V_7O_{16} unit cell, as shown in Fig. 3 b). Due to asymmetric and weak bonding of vanadium (V5) atoms, vanadium oxides are borne to form twin-plane structures to compensate the charge in equilibrium. One twin-plane is depicted in Fig. 3 b) by a blue dashed line. The channels formed by these planes are found to be responsible for high response, when material is used as a gas sensor [12]. This could be due to new bondings formed by NH_3 molecules between the V_7O_{16} sheets, in a similar way as the amines in VO_x -NT structures.

Figure 3. Lattice models used in Rietveld refinement calculations for vanadium oxide thin films: **a)** orthorhombic $Pmmn$ V_2O_5 phase and **b)** triclinic $P-1$ V_7O_{16} phase.

The grazing incidence diffraction (GID) X-ray diffraction patterns, Rietveld refinement fittings and the fitting residuals of the three different types of vanadium oxide thin-film structures are shown in Fig. 4. Fitting results clearly show the existence of both orthorhombic V_2O_5 and triclinic V_7O_{16} phases in all thin films, only the dominance between the two phases varies in compositions of the different films. In Fig. 4 a), XRD data of the film with a dominating V_2O_5 phase mixed with a minor V_7O_{16} phase is presented. Fig. 4 b) presents XRD data of the film with about equal presence of the two phases in the films composition. Finally, XRD data of the film with a dominating V_7O_{16}

phase is shown in Fig. 4 c). In Table 1, the main Rietveld refinement fitting parameters of one of the three vanadium oxide thin-film structures are presented together with reference parameters gained from the literature. All of the fittings were made within a fitting accuracy with $RWP = 5.47\%$ and $\chi^2 = 1.24$ in Fig. 4 a), $RWP = 10.68\%$ and $\chi^2 = 2.21$ in Fig. 4 b), and $RWP = 11.58\%$ and $\chi^2 = 1.22$ in Fig. 4 c).

The calculated Rietveld refinement results are in very good agreement with the measured data in the two thin-film structures presented in Figs. 4 a) and b). The measured XRD curves have high intensities and thus also the fitting could be done more accurately. However, the measured XRD result presented in Fig. 4 c) has a low intensity in the peaks present and also the background noise is higher than in the results in Figs. 4 a) and b). These properties make the Rietveld refinement calculations more challenging for the thin-film with majority V_7O_{16} phase in the structure, and thus also the residual values are much higher. However, the lattice model of triclinic V_7O_{16} fitted well to all of the measured XRD result, as can be seen from the main peaks in the curve, *e.g.* $2\theta \sim 24.9^\circ$. Also, other common vanadium oxide phase structures were studied in the context of the XRD and Raman data analysis, *e.g.*, VO_2 , V_6O_{13} , V_2O_3 , and V_4O_9 . However, when both the Raman and Rietveld refinement results are taken into account, these other phases did not fit to the gained measurement results. Thus, as a conclusion, it can be said that the results presented here point very strongly to the co-existence of both V_2O_5 and V_7O_{16} phases in the thin-film structures. When fitted unit cell lattice constants are compared to bulk materials values found in the literature, as shown in Table 1, it is observed that lattice constants are typically shorter for the nanostructured films. This is most likely due to substrate interface or deposition process generated compressive residual stress in the films.

Generally, Rietveld refinement is also used to quantify the concentrations of different materials in, *e.g.* ceramic powders. However, with thin films, where there are so many different properties affecting the X-ray diffraction curve, for example strains between the substrate and thin film and orientation effects of the thin film, it is often more difficult and inaccurate to quantitatively

calculate the phase composition of the film. As also in this particular case, Topas software uses every possible reflection of the crystal structures studied, which in this case are orthorhombic V_2O_5 and triclinic V_7O_{16} , in the quantitative phase composition calculation. Obviously, the triclinic vanadium oxide phase has a much larger number of reflections in the 2θ -angle region studied than the orthorhombic phase, which can lead to situation in which the amount of V_7O_{16} phase is over estimated in the quantitative analysis. However, this problem can be minimized by taking care that only the (hkl) reflections found in the measured XRD data are included in the Rietveld calculations for each detected phase, and the effect of noise is carefully diminished (data presented in Fig. 4 c). After such quantitative Rietveld calculations, results are quite well in concurrence with the Raman measurement data presented previously. For the major V_2O_5 film, the quantitative result was 67% of V_2O_5 phase and 33% of V_7O_{16} , for the more equal mixture of the two phases according to Raman measurements, the result was 45% of V_2O_5 phase and 55% of V_7O_{16} , and for the film with major V_7O_{16} phase 15% of V_2O_5 phase and 85% of V_7O_{16} .

Figure 4. The measured GID XRD data with calculated Rietveld refinement results of the vanadium oxide thin films: **a)** film with a dominating orthorhombic V_2O_5 phase, **b)** film with equal mixture of orthorhombic V_2O_5 phase and triclinic V_7O_{16} phase, and **c)** film with dominating triclinic V_7O_{16} phase.

RWP (%) = 5.47, $\chi^2 = 1.24$	V_7O_{16}	V_2O_5	V_7O_{16} [5]	V_2O_5 [24]
Spacegroup	P-1	Pmmn	<i>P-1</i>	<i>Pmmn</i>
Lattice parameters				
<i>a</i> (Å)	6.06	11.48	6.16	11.51
<i>b</i> (Å)	6.12	3.56	6.17	3.56
<i>c</i> (Å)	19.36	4.38	19.11	4.37
<i>alpha</i> (°)	96.39	90	96.14	90
<i>beta</i> (°)	92.87	90	92.82	90
<i>gamma</i> (°)	89.48	90	90.07	90
Cell Volume (Å³)	712.3	178.9	721.5	179.2

Table 1. The main Rietveld refinement fitting parameters of one of the three vanadium oxide thin-film structures with reference parameters from the literature.

3.2 Microstructure of the thin films

Cross-section microstructure studies were made by transmission electron microscopy (TEM). In Fig. 5 a), TEM micrograph of the thin film with dominating V_2O_5 phase is presented. The film shows a clear polycrystalline structure with only minor fiber or tubular-like structures. Also, the film seems to be very dense without any pores. TEM micrographs of the film with structure of both V_2O_5 and V_7O_{16} phases are presented in Figs. 5 b) and c). Cross-section micrographs show a strong porosity in the thin film structure, and also the strong existence of clear fiber or tubular-like textured nanostructures. In Figs. 5 d) and e), TEM micrographs of the film with dominating V_7O_{16} phase are presented. Cross-section micrographs show now again dense polycrystalline structure. The fiber or tubular-like nanostructures with multi-layered fine structure, as shown in Fig. 5e), are now very distinctive and strong in this film. This could be expected according the results from Raman spectroscopy and XRD measurements, assuming that the amount of triclinic V_7O_{16} phase is comparable to the amount of fiber or tubular-like nanostructures in the film composition. With this

assumption, the existence of these fine structures is another evidence of the presence of triclinic V_7O_{16} phase in the thin films. However, it should be pointed out, that these structures differ from the conventional vanadium oxide nanotubes, VO_x -NTs, because of the manufacturing method. In PLD process, as compared to chemical precipitation, there are no organic substances present in the growth process, only oxygen gas and a pure ceramic V_2O_5 target in vacuum conditions. Hence, it is clear that the fiber or tubular-like structures here are composed solely of V_7O_{16} solid state phase. It has been suggested elsewhere [5], that the reason for the tubular-like morphology of V_7O_{16} is reduction of V^{5+} ions to V^{4+} of the VO_5 tetrahedra structure in the V_7O_{16} crystal. Vanadium V^{4+} ions are much larger in size than V^{5+} , and thus the size of one side of V_7O_{16} layer will increase, causing the tendency to form tubular structures of the layers. As a conclusion from the microstructural studies made by TEM, it was observed that the films have much more porous structure when the two phases V_2O_5 and V_7O_{16} are equally mixed in the same film when compared to the denser films with either V_2O_5 or V_7O_{16} phase dominating the composition. Also, the existence of fiber or tubular-like nanostructures is largest in films with a strong presence of V_7O_{16} phase.

Figure 5. TEM cross-section images of **a)** film with a dominating orthorhombic V_2O_5 phase, **b)**, **c)** film with equally strong orthorhombic V_2O_5 phase and triclinic V_7O_{16} phase, and **d)**, **e)** film with dominating triclinic V_7O_{16} phase.

3.3 Surface potential and morphology

Atomic force microscopy (AFM) and Kelvin probe method were utilized to measure surface morphology and surface potential maps of the films with different compositions. The potential maps present the difference between the work functions of the platinum AFM tip and the thin film surface, *i.e.* $\Delta\Phi = \Phi_{Pt} - \Phi_{film}$, and thus mV scale in the potential maps in Fig. 6 equals to meV scale of work function. The section graphs show the surface potential value along the red line drawn in surface potential maps. In all the thin film surfaces, the existence of particulate droplets produced in PLD process can be seen as bright white spots in morphology micrographs. In Fig 6 a), the morphology and potential graphs of the film with a dominating V_2O_5 phase are shown. The micrographs show a smooth film surface with rms roughness $R_q \approx 14.2$ nm. The surface potential map follows the variation of the surface height in the case of large variations like droplets, otherwise the potential map is quite smooth, with value of $\Delta\Phi \approx -150$ meV. In Fig. 6 b), the micrographs and data of the film with equal mixture of both V_2O_5 and V_7O_{16} phases are presented. The surface is now rougher with rms roughness $R_q \approx 28.3$ nm. Also, the surface potential map shows the phase composition variations between V_2O_5 phase as darker areas and V_7O_{16} phase as lighter areas, respectively. It is also obvious, that surface potential map is distinctively different from the surface morphology in Fig. 6 a), and thus do not follow the variation of sample surface height profile. This proves that there are two different phases with two different work functions existing in the thin-film surface. The morphology and potential maps of the film with dominating V_7O_{16} phase are shown in Fig. 6 c). In this case, the surface is also quite smooth with $R_q \approx 14.6$ nm. The surface potential value follows the surface morphology in the same way as in the case of

dominating V_2O_5 film in Fig. 6 a). However, average surface potential value $\Delta\Phi \approx -110$ meV differs from the film with a strong V_2O_5 phase by about ≈ 40 meV. This directly demonstrates the ≈ 40 meV difference in work function values of the two films with dominating V_2O_5 and V_7O_{16} phases, and thus also proves the different work functions of the two phases. It should be pointed out here, that as the orthorhombic V_2O_5 phase is proven to be *n*-type semiconductor, the triclinic V_7O_{16} is shown to have *p*-type behaviour [25,7].

As a conclusion from the AFM surface morphology and potential data, it is shown that when the two phases V_2O_5 and V_7O_{16} are equally mixed together to the same film composition, the surface gets much rougher and the film more porous, as compared to the smoother surfaces seen in the single phase films. Also, the surface potential measurements clearly proved the existence of two different separate phases in thin films by showing the two different work function values of the thin films with dominating V_2O_5 and V_7O_{16} phases.

Figure 6. AFM surface morphology micrographs (left), surface potential maps (middle), and section graphs of the surface potential maps along the red lines of **a)** film with a dominating orthorhombic V_2O_5 phase, **b)** film with mixture of both orthorhombic V_2O_5 phase and triclinic V_7O_{16} phase, and **c)** film with dominating triclinic V_7O_{16} phase.

3.4 Ammonia gas sensing properties

The porous mixed phase thin-film structures with V_2O_5 and V_7O_{16} were also deposited on oxidized silicon substrates to study their chemical sensing properties, especially towards ammonia NH_3 gas. The films deposited on oxidized silicon were made intentionally thinner than the ones

made for the structural characterization on sapphire substrates. Making the films thinner in this way is known to enhance their gas sensing properties. Also, a minor change in the morphology of the sensing layers was noticed when the substrate was changed, but the vanadium oxide phase composition could still be tuned in a similar way regardless of the substrate used. The change in the surface morphology of the films, reason for this being most probably the change of the substrate material, clearly enhanced the gas sensitivity of these layers. These observations have also been reported in our previous studies [11,16]. Thus it can be concluded, that the change of substrate material from Al_2O_3 to oxidized silicon, and varying the film thickness, has mainly effect on the surface morphology of films, but not on the crystalline structure or phase composition. This is due to accurately adjusted PLD conditions including *in-situ* heat treatment procedure and oxygen partial pressure $p(\text{O}_2)$.

Also, it was shown in our earlier studies [11,16], that when the phase composition in the thin film is tailored to an optimum ratio between the V_2O_5 and V_7O_{16} phases, the response to gases, especially to NH_3 , reaches its highest value. Also, the selectivity of such films towards ammonia was clearly improved, for example, in comparison to nitrogen oxides (NO_x) and carbon monoxide (CO), gases typically present in diesel engine exhaust after SCR process. Sensors prepared of mixed phases of V_2O_5 and V_7O_{16} could clearly follow ppm-range changes of NH_3 despite of different levels of NO_x interferences in the background, and also the detection limit of such sensing materials to CO (≈ 50 ppm) was clearly higher than to NH_3 (≈ 40 ppb) [16]. However, when the film is composed almost solely of one phase, the sensitivity is decreased. On the other hand, it was also found that the pure V_2O_5 phase film is more electrically and thermally stable than the films with more mixed phase structures [16]. The reason for this is most probably the higher amount of oxygen vacancies due to the presence of certain amount of V_7O_{16} in the films, which then causes instability at higher temperatures. When the film is composed of pure V_2O_5 phase, the valence states of the film contain almost totally only V^{5+} ions. But when an increasing amount of V^{4+} ions is introduced to the structure with the V_7O_{16} symmetry, the amount of oxygen vacancies is increased, causing an

increase in the gas response, but on the other a decrease in the stability at higher temperatures. Also, it was shown in Ref. [11] that the V_7O_{16} phase, at certain conditions, behaves like a p -type semiconductor, while the pure V_2O_5 is known as n -type semiconductor. This causes the existence of p - n junction grain boundaries in the films where a suitable amount of both phases are mixed together. The existence of the p - n junctions leads to higher baseline resistance, which also can lead to higher gas responses. When the p -type V_7O_{16} is the dominant phase, the resistance level is again lower, which causes also a decrease in the gas response.

The films deposited on silicon have proven to be extremely sensitive to ammonia down to ≈ 40 ppb concentration, and also to large extent, selective to ammonia when compared to nitric oxide NO up to 20 ppm and carbon monoxide CO up to 50 ppm [16]. These are very important properties needed in gas sensors controlling the selective catalytic reduction (SCR) process used in diesel truck engines. In the process, urea, which forms ammonia, is used to reduce the produced toxic NO/NO₂ gas in the catalytic converter of the truck exhaust system to harmless nitrogen and water [26]. It has been suggested elsewhere, that layered, more open framework crystal structures, *e.g.* hexagonal WO₃, are very suitable for detection of ammonia gas, the reason being the reaction of lattice oxygen of the metal oxide with the measured gas, and easy mechanisms for adjusting the unstoichiometric metal to oxygen ratio [27,28]. As was already mentioned in the introduction, also V₂O₅ and V₇O₁₆ are formed of layered structures and thus should be considered as highly potential ammonia sensing materials.

An example of a gas response with ammonia gas concentrations at ppb-levels is shown in Fig 7. The measurement temperature was 350 °C and the gas injection and dwell time was 2 hours. It can be seen that the sensor shows a clear response already at 200 ppb level of ammonia. However, there is a small drift present in the resistance baseline and also the response time is not very fast. Yet, types of vanadium oxide thin-film structures have been proven to be a promising candidate as a material for ammonia gas sensors [16].

Figure 7. The sensor signal, measured as the resistance, of the mixed phase, $V_2O_5 + V_7O_{16}$, during exposure to NH_3 at ppb-level concentrations. The measurement was performed at $T = 350^\circ C$ and with 20 % of O_2 in N_2 as a carrier gas.

4. Conclusions

A thorough structural study of pulsed laser deposited vanadium oxide thin films was performed. X-ray diffraction and Raman spectroscopy results showed the co-existence of orthorhombic V_2O_5 phase, and a phase usually seen in vanadium oxide nanotubes (VO_x -NTs). Rietveld refinement performed on the XRD data confirmed two crystal structures of orthorhombic V_2O_5 phase and triclinic V_7O_{16} phase. Triclinic V_7O_{16} phase is previously only found in layered wall structure of VO_x -NTs with a chemical amine between the V_7O_{16} phase twin-plane layers. The transmission electron microscopy studies supported XRD and Raman spectroscopy results by proving that all the thin films had polycrystalline structure, and also fiber or tubular-like nanostructures were found, especially in the film compositions containing the V_7O_{16} phase. When the film was composed of

equal mixture of both phases V_2O_5 and V_7O_{16} , the microstructure was very porous and the surface especially rough. The measured surface potential values showed the clear difference in the work functions of the two phases of about ≈ 40 meV. The films were also tested as a possible sensing material for ammonia gas, and response to NH_3 was seen already at ppb-levels of gas concentration.

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